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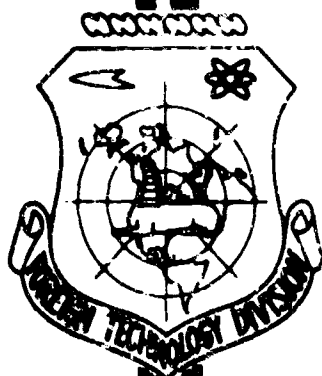
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TRANSLATION

CHEMISTRY OF SULPHUR ORGANIC COMPOUNDS CONTAINED IN PETROLEUM
AND PETROLEUM PRODUCTS (SELECTED ARTICLES)

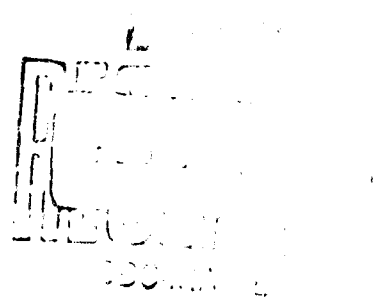
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EDITED MACHINE TRANSLATION

CHEMISTRY OF SULPHUR ORGANIC COMPOUNDS CONTAINED IN PETROLEUM
AND PETROLEUM PRODUCTS (SELECTED ARTICLES)

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TABLE OF CONTENTS

Influence of Organic Sulfur Compounds on Exploitation Properties of Fuel TS-1, By Ya. B. Chertkov, V. M. Shchagin and V. N. Zrelov.....	1
Influence of Natural and Synthetic Sulphur and Nitrogen Containing Compounds on the Thermooxidizing Stability of Direct Distillation of Fuels, By G. F. Bol'shakov, P. I. Davydov, T. G. Potapenko, F. Yu. Rachinskiy and N. M. Slavachevakaya.....	17
Investigation of the Thermal Stability and Corrosiveness of Sulfurous Fuels at Temperatures Above 100 C, By Ye. R. Tereshchenko and M. Ye. Tararyshkin.....	32

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INFLUENCE OF ORGANIC SULFUR COMPOUNDS ON EXPLOITATIONAL PROPERTIES OF FUEL TS-1

Ya. B. Chertkov, V. M. Snchagin, and V. N. Zrellov

The sulfur content (organic sulfur compounds) in oil products produced from sulfurous oils is strictly regulated by GOST norms. Thus, in fuel TS-1 (GOST 7149-54), the content of total sulfur must not exceed 0.25%, and mercaptan - 0.01%.

During research on the variations of the exploitational properties of fuels sulfur organic compounds are considered independently of their structure as part of the non-hydrocarbon impurities. Mercaptans are an exception. However, it is difficult to assume that all organic sulfur compounds, regardless of their structure, have an identical negative influence on the quality of a fuel.

The present investigation was undertaken for the purpose of studying the influence on the exploitational qualities of contemporary fuels of type T of sulphur organic compounds (in quantities allowed by GOST 7149-54), taking into account their structure.

Studies were made of 23 individual organic sulfur compounds* of various structure, the presence of which in fuel of type T, judging by their molecular weights and boiling points, is very probable, and studies were also made of

*The organic sulfur compounds and concentrates were obtained at the Institute of Organic Chemistry of the Bashkir Branch of the Academy of Sciences of the USSR (BashPAN SSSR).

concentrates separated from fuel TS-1 (see table). Hydropurified fuel TS-1, not containing organic sulfur compounds and thermally stable at a temperature of 250°C (limiting temperature, at which the tests were conducted) served as a background. Into hydropurified fuel TS-1 were introduced different quantities of organic sulfur compounds not exceeding (in sulfur) the norms permissible by GOST 7149-54. The mixtures were heated for 6 hours during mixing in autoclaves made of EYa-1T brand steel and half loaded (the remaining volume was filled by air). Two plates of brand VB-23NTs bronze were in contact with a total surface of 0.002 m²/100 ml of fuel. The fuel mixing was produced by bronze plates suspended from a revolving cartridge for thermocouple. Tests were conducted at 120°, 150°, 200°, and 250°C.

In the course of the tests determinations were made of the corrosion of bronze, resin depositing on the metallic plates, and of the quantity and magnitude of insoluble deposit particles formed in the fuel. With the help of an electronic microscope we managed to obtain, in general form, the mechanism of solid phase formation in a heated fuel in presence of organic sulfur compounds.

1. Corrosion

Corrosion of VB-23NTs bronze was characterized by loss of weight of metal in g, relative to 1 m² surface. Before the test the bronze was ground to mirror brightness on a wheel, which was covered by a cloth and coated with a layer of No. 1 paste from the State Optical Institute (dimensions of particles 7-10 μ). Then the plate was washed in alcohol-benzene mixture and isopentane, dried, and weighed on analytic scales. After the test in fuel and washing in the alcohol-benzene mixture the bronze was weighed. The difference in weight constituted the loss from corrosion. The grinding did not completely remove the residual scratches from the surface of the metal. After test in fuel containing organic sulfur compounds, and separation of the tarry-fuel layer, the surface of metal obtained a completely

Physicochemical Properties of Organic Sulfur Compounds (According to
Data of the Institute of Organic Chemistry, BashFAN SSSR)

Organic sulfur compounds	Boiling point, °C (pressure, mm Hg)	Index of re- fraction n_D^{20}	Density ρ_4^{20}
Mercaptans			
Isoamyl-mercaptan.....	115-118 (754)	1.4426	0.8360
Secondary octyl-mercaptan.....	186-187 (758)	1.4485	0.8429
Methylcyclohexyl mercaptan.....	74-75 (17)	1.4838	1.0110
Benzylmercaptan.....	64-66 (4)	1.5757	1.0544
α -thionaphthol.....	151-153 (20)	—	1.1547
Sulfides			
Dibutylsulfide.....	91-92 (10)	1.4532	0.8440
Di-isobutylsulfide.....	83-85 (30)	1.4470	0.8263
Butyl-secondary-octylsulfide...	119-120 (8)	1.4580	0.8429
Di-secondary-octylsulfide.....	135-136 (2)	1.4610	0.8403
Ethylmethylcyclohexylsulfide...	65.5-60 (10)	1.4649	—
Isoamylmethylcyclohexylsulfide.	133-136 (15)	1.4760	0.8995
Methylbenzylsulfide.....	87-88 (6)	1.5630	1.0274
Dibenzylsulfide.....	T. nn 48.5-49	—	—
Thiophanes			
α -Propylthiophane... ..	144-178 (740)	1.4862	0.9307
α -(3-methylbutyl) thiophane....	215-216 (768)	1.4840	0.9176
α -Amylthiophane.....	224-225 (762)	1.4828	0.9131
Thiophenes			
Thiophene.....	83-84 (760)	1.5289	1.0652
α -Butylthiophene.....	80-81 (22)	1.5019	0.9535
α, α' -Dibutylthiophene.....	87-89 (2)	1.4942	0.9181
Dibenzothiophene.....	T. nn 98-99	—	—
Disulfides			
Di-isobutyldisulfide (2.7- dimethyl-4.5-dithiooctane)...	108.5-109 (13)	1.4842	0.9272
Di-secondary-octylsulfide (5.8-dipropyl-6.7-dithiado- decane).....	197-198 (7)	1.4818	0.8982
Di-o-tolylsulfide.....	T. nn 37.5-38	—	—
Sulfurous concentrates, separated from fuel TS-1			
Sulfur content 4.3%.....	150-200 (760)	—	—
Sulfur content 17.96%.....	187-240 (760)	1.4852	—

different character. At a 500-fold magnification blisters and pitted sections were very conspicuous even where the loss of weight of metal was insignificant (Fig. 1).

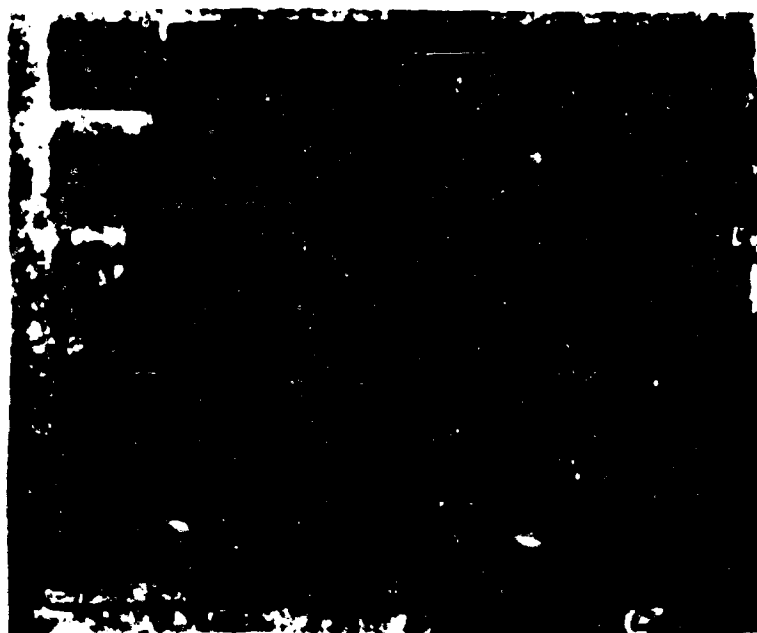


Fig. 1. Bronze VB-23NTs after heating in hydropurified fuel TS-1 containing sulfurous compounds (magnified 500 times).

a—0.01% weight mercaptan sulfur: 1—fuel without mercaptans; 2—isoamylmercaptan; 3—secondary-octylmercaptans; 4—benzylmercaptan; 5— α -thionaphthol.

b—0.25% weight. S sulfurous concentrates and acyclic sulfides: 1—sulfurous concentrate separated from fuel TS-1 (S = 4.3%; t_k = 150–200°C); 2—sulfurous concentrate separated from fuel TS-1 (S = 17.96%; t_k = 187–240°C); 3—dibutylsulfide; 4—di-isobutylsulfide; 5—butyl-secondary-octylsulfide.

c—0.025% weight S thiophenes, thiophenes, and disulfides: 1— α -amylthiophane; 2—thiophene; 3— α -butylthiophene; 4—di-secondary-octylsulfide; 5—di-o-tolyldisulfide.

From the figure it is clear that with increase of the test temperature, in the presence of sulfur organic compounds, in all cases, the affected surface area of the metal increases.

Of the mercaptans (0.01% of sulfur*) the strongest influence on bronze was rendered by compounds with an aromatic ring - benzylmercaptan and α -thionaphthol.

*In the present article subsequently the concentration of organic sulfur compounds will everywhere be given in terms of sulfur.

Even after heating at a temperature of 150°C the surface of the metal was thickly covered by dark spots. Mercaptans of aliphatic and naphthenic structure (in the same quantity) led to insignificant changes in the surface of the metal. Organic sulfur compounds of other classes, especially di-o-tolyldisulfide (0.25%), evoked a significant change in the surface of bronze. Such is the picture based on visual observations, which are confirmed by the results of quantitative appraisal of loss of weight of the metal.

In the reference fuel during heating to 250°C the loss of weight of bronze was insignificantly small and was within the limits of sensitivity of the method (0.2 g/m^2).

Mercaptans. For the mercaptans, introduced into the fuel in quantities of 0.0012 and 0.0025%, at a temperature of heating to 200°C the loss of weight of bronze did not differ from the loss in the reference fuel under the same conditions.

With increase of the concentration of mercaptans to 0.01% the loss of weight of bronze increased as compared to loss in the reference fuel by 3 times at 120°C and by 1.5 times at 150° and 200°C. In contrast to this, in the fuel with benzylmercaptan at 200°C the loss of weight of bronze increased 13 times, and in the fuel with methylcyclohexylmercaptan at 200°C the loss of weight of bronze did not differ from the loss in the reference fuel.

Sulfides. Sulfides in fuel (0.12%) at heating to 150°C are low-active with respect to brand VB-23NT's bronze. At 200°C the loss of weight of bronze increases 3 times as compared to the loss in the reference fuel under the same conditions.

At a concentration of 0.25% sulfides at a temperature of 150°C the loss of weight of bronze increases by 4-5 times, and at 200°C - by 1.5-5 times.

Disulfides. At a concentration of disulfides of 0.25% at 150-200°C an increase of weight loss of bronze of 2-3 times occurs as compared to the loss in the reference fuel. In the presence of 0.12-0.25% di-o-tolyldisulfide at 150°C the corrosion losses increased by 50-70 times.

Thiophenes. At a concentration in fuel of 0.12% and at a temperature of heating up to 200°C, thiophenes do not cause a noticeable weight change in bronze. At concentration 0.25% and a temperature of 150°C the losses increase by 1.5-2 times, but at 200°C - by 2-3 times as compared to losses in the reference fuel.

Thiophenes in concentration of 0.25% and at heating to 250°C are not corrosionally active. The loss of weight of bronze is insignificantly small.

Sulfurous concentrates of fuel TS-1 in a concentration of 0.25% and at a temperature to 200°C do not evoke increased losses of bronze as compared to losses of bronze as compared to losses in the reference fuel.

Thus, corrosivity of organic sulfur compounds in fuel with respect to bronze is small when their concentrations are within the limits allowed by the GOST and temperature of heating of the fuel is 200-250°C. The exception is di-o-tolyl-di-sulfide, which proved to be very active. Thiophenes are inactive and in this they favorably differ from other organic sulfur compounds.

2. Resin Formation

The tarry substances which adhered to the surface of bronze VB-23NTs in the process of heating the fuel and were separated only by washing the plate with an alcohol-benzene mixture (1:1) were not dissolved in the isopentane, which was used to separate the fuel. Therefore, the weight of the tarry deposits on the bronze was estimated to be the difference in weight of the plate after treatment with isopentane and the alcohol-benzene mixture. The weight of tars was related to 1 m² surface of bronze. The sensitivity of the method of determination was 0.2 g/m².

Mercaptans. During the introduction into hydropurified fuel TS-1 of mercaptans in concentration to 0.01% and heating of the mixture to 200°C the quantity of resins on the surface of the bronze of brand VB-23NTs was insignificant, and the fuel mixture by this index did not differ from hydropurified fuel TS-1. The exception

was aromatic mercaptans. During heating to 200°C and at a concentration of 0.005% in the presence of thionaphthol, the quantity of resins increases 1.5 times, and in the presence of benzylmercaptan - by 3 times. At a 0.01% concentration of these mercaptans tarry precipitate at 200°C in the presence of thionaphthol increase by 2 times, but in the presence of benzylmercaptan - by 15 times as compared to the reference fuel.

Sulfides. Sulfides led to significantly larger precipitate of resins on the surface of bronze than did the mercaptans. Thus, at a concentration of 0.12% and a temperature of 150°C the quantity of tarry precipitate increased 2-3 times, and for certain sulfide even more, as compared to the quantity of tarry precipitate in the reference hydropurified fuel. It is interesting that in the presence of aromatic sulfides (methylbenzylsulfide, dibenzylsulfide) the quantity of tarry precipitate did not increase. Thus, the aliphatic and naphthenic sulfides played a negative role. With an increase of the concentration of sulfide to 0.25%, at 150°C the picture was changed insignificantly; with further heating to 200°C the quantity of tarry precipitate increased 6-12 times as opposed the quantity observed for the reference fuel. At 200°C aromatic sulfides also gave a significant quantity of tarry precipitates.

Disulfides. At a disulfide concentration of 0.25% and temperature of 150°C the quantity of tarry precipitate increased by 3 times, at 200°C - by 4 times, and at 250°C - by 8-16 times as compared to their quantity in the reference fuel. An especially large number of resins was formed in the presence of di-o-tolyldisulfide at 150°C.

With increase of the fuel temperature disulfides, mainly aromatic ones, underwent condensation and closely adhered to the surface of bronze VB-23B.

Thiophanes. At a content of up to 0.25% in hydropurified fuel and during heating to 200°C the thiophanes exerted a small influence on the formation of tarry

precipitates, which increase by 1.5-2 times.

Thiophenes in concentrations up to 0.25% during heating of the fuel to 250°C do not give tarry precipitates on bronze VB-23NTs.

Sulfurous concentrates of fuel TS-1 with boiling limits of 150-200°C in concentrations up to 0.25% and during heating to 200°C did not give tarry precipitates on the bronze. In contrast, sulfurous concentrates, which boil within the limits 187-240°C, under the same conditions led to a twofold increase in precipitate as compared to the reference fuel.

Thus, the greatest sources of tarry precipitate formations on bronze VB-23NTs are sulfides and disulfides during heating of the fuel from 150°C and above. Thiophenes during heating of the fuel to 250°C do not give tarry secession.

3. Sedimentation

The deposits constituted solid particles, retained on a No. 4 glass filter after filtration of the fuel, which had been subjected to a 6-hour heating in an autoclave in contact with the bronze. The deposits were washed on to a filter with isopentane and brought to a constant weight at room temperature. The sensitivity of the method was 0.2 milligrams per 100 ml of fuel (the convergence of parallel determinations was ± 0.25 milligram/100 ml).

Mercaptans. Heating the fuel with mercaptans (in concentrations 0.0012-0.01%) at 120°C led to the formation of a deposit (0.5-2.5 milligram/100 ml), while in the hydropurified fuel there was none. At 150-200°C 2-3 times more deposit was formed than in the reference fuel.

Sulfides. At 150°C (temperature of maximum sedimentation) sulfides in concentrations of 0.12% lead to an increase in deposit of 3-7 times, and at 0.25% of 4-9 times. At a higher temperature (200°C) the quantity of deposit is lowered somewhat and exceeds the quantity of deposit formed in the reference fuel by 4-5

times. This is in keeping with the character of sedimentation in commercial fuels, which form a maximum quantity of deposit at 150°C, but which experience a drop in the weight quantity of deposit at higher temperatures as a result of simultaneous condensation and enlargement of the particles.

Disulfides. In the presence of aliphatic disulfides in concentrations of 0.25% the quantity of deposit at 150°C increases by 3-6 times, at 200°C by 2-4 times, and 250°C by 2-3 times as compared to the deposits in the reference fuel under the same conditions. A huge quantity of deposit (50 times more than for the reference) is obtained at 150° in the presence of di-o-tolyldisulfide.

Thiophanes. In the presence of thiophanes in concentrations of 0.25% at 150°C the quantity of fuel deposit increased by 4-6 times, at 200°C by 3-4 times, i.e., in this respect thiophanes are analogous to aliphatic disulfides.

Thiophenes. The presence of thiophenes in concentrations of 0.25% at 150-200° increases the deposit by 1.5-2 times, but at 250°C it does not evoke sedimentation.

An exception is α, α' -dibutylthiophene, in presence of which (apparently, from its two side chains) at 150°C 6 times more deposit was formed, and at 200°C - 4 times more than in the reference fuel.

Sulfurous concentrates of fuel TS-1. Organic sulfur compounds of concentrates in quantities of 0.25% led to an increase of deposit at 150-200°C by 2-4 times as compared to deposits in the reference fuel. In Fig. 2 are shown deposits forming under the action of organic sulfur compounds at 500-fold magnification.

From the figure it is clear that the density and area occupied by the deposits which are formed by the action of mercaptans, increase with increases in the temperature of heating of the fuel, especially in the case of thionaphthol and secondary-octylmercaptan.

In the presence of acyclic sulfides, thiophanes, and disulfides at 150-200°C an abundant dense deposit will form as large aggregates of cohering particles. In

contrast, in the presence of thiophenes and concentrates of organic sulfur compounds of fuel TS-1 the deposit consists of small particles of small density.



Fig. 2. Deposits formed in hydropurified fuel TS-1 in the presence of sulfur compounds (magnified 500 times).

a—0.01% weight mercaptan sulfur: 1—isoamylmercaptan; 2—secondary-octylmercaptan; 3—methylcyclohexylmercaptan; 4—benzylmercaptan; 5—thionaphthol.

b—0.25% sulfurous concentrates and acyclic sulfides: 1—sulfurous concentrate, separated from fuel TS-1 ($S = 4.3\%$; $t_k = 150-200^\circ\text{C}$); 2—sulfurous concentrate, separated from fuel TS-1 ($S = 17.96\%$; $t_i = 187-240^\circ\text{C}$); 3—dibutylsulfide; 4—di-isobutylsulfide; 5—butyl-secondary-octylsulfide.

c—0.25% thiophanes, thiophenes and disulfides: 1— α -amylthiophane; 2—thiophene; 3— α -butylthiophene; 4—di-secondary-octyldisulfide; 5—di-o-tolyldisulfide.

Thus, at a temperature $150-250^\circ\text{C}$ acyclic sulfides, thiophanes, and disulfides at concentration of 0.25% cause the formation of significant quantities of deposit. The maximum quantity of deposit was observed at a temperature of 150°C .

Along with the weight quantity of the deposit in the fuel the screen composition, or magnitude of the particles making up the deposit is of great importance for normal use by the fuel system of a motor. Actually, a deposit may be of small weight, but its particles so big that they are retarded and clog the filtering

elements, restricting or stopping the entrance of fuel into the zone of combustion. The reverse picture is possible as well where significant quantity of deposit is formed but the dimensions of its particles are so small that they freely penetrate through the filtering elements, proceed with the fuel into the zone of combustion and burn, causing no complications. As an example, consider a stabilized colloidal system, which, as is known, is characterized by particle dimensions of up to 1μ .

We tried to estimate the influence of individual sulfur organic compounds on the magnitude of particles of the deposit forming during heating of the fuel.

For that the fuel being heated was passed through a calibrated filter of square weave. After washing the filter with isopentane and drying, the quantity of deposit (in %), retained by filter was determined by the difference between the weight of the filter with deposit and without it. In the operation a set of filters with holes of different dimensions was used. However, we shall mention only the share of deposit, retained by two filters: with holes 15 and 50μ . These filters are close to those applied in practice, and the data obtained shows what part of the deposit is obtained with particles larger than 15 and 50μ .

Mercaptans. At a temperature of heating of 120°C in the fuel with mercaptans (to 0.01%) particles of the deposit are very fine. The whole deposit passed through a filter with 15μ holes. With an increase in the temperature the particle increased significantly in size. In the presence of 0.01-0.0025% thionaphthol 42-50% of the deposit did not pass through the filter with 15μ holes and 5-6% — through the filter with 50μ holes. Under the same conditions in presence of aliphatic and naphthenic mercaptans 10-20% of the deposit constituted particles of more than 15μ dimensions and particles of 50μ dimensions were almost absent. At 200°C and 0.01% content of both aliphatic and aromatic mercaptans deposit with big particles was formed: 50-90% with particles larger than 15μ and 4-6% — with particles larger than 50μ . Only in the presence of methylcyclohexylmercaptan and

benzylmercaptan were almost all of the particles of the deposit smaller than 15μ .

Thus, the biggest deposit particles are obtained in the presence of thionaphthol (150°C and above) and aliphatic mercaptans (200°C) and the finest - in the presence of benzylmercaptan and methylcyclohexylmercaptan (200°C).

Sulfides. In fuel, containing 0.25% sulfur sulfide, at 150°C deposits are obtained in which 12-25% of the particles are larger than 15μ , and 2-8% of the particles are larger than 50μ . At 200°C the particle magnitude is not changed significantly.

Disulfides. Within the limits $150-250^{\circ}\text{C}$ and at a concentration of 0.01% sulfur disulfide, 15-25% of the deposit consists of particles larger than 15μ and 4-14% - larger than 50μ .

Thiophanes. In the presence of thiophanes at a temperature of $150-200^{\circ}\text{C}$ part of the deposit (20-60%) has particles which are larger than 15μ . Deposit with particles larger than 50μ constitutes 3-9%.

Thiophenes. In the presence of thiophenes a light-weight and very fine deposit will form. Thus, at $150-250^{\circ}\text{C}$ the portion of particles larger than 15μ constitutes in all 0.25% of the deposit, and particles smaller than 50μ are absent.

Sulfurour concentrates of fuel TS-1. In the temperature interval $150-200^{\circ}\text{C}$ 8-25% of the deposit consists of particles larger than 15μ and up to 8% of particles larger than 50μ .

Thus, the magnitude of the deposit particles depends on the concentration of organic sulfur compounds, their chemical structure, and the temperature of heating of the fuel. Exceptions are thiophenes, which even at a temperature of 250°C gave an insignificant quantity of deposit with very fine particles.

4. The Mechanism of Sedimentation

Samples of the fuels were examined before and after the heating test on a.

Em-3* electron microscope with a resolving power of 60 \AA at a magnification of 10,000 times. As a preliminary the samples were thoroughly filtered: the absence of a visible solid phase was controlled on a MM-8 microscope with a magnification of 100 times.

For the electron microscope average fuel sample applied on the collodion sublayer was placed in vacuum apparatus at a residual pressure of $1 \cdot 10^{-5} \text{ mm Hg}$ for 4-6 hours (till full evaporation of the fuel). After such preparation the samples were examined on an electron microscope and different sections of them were photographed.

The obtained photographs are shown in generalized and systematized forms in Figs. 3 and 4. Photographs of fuels with impurities of different organic sulfur compounds (0.01-0.25%) differed in no way from photographs of the reference fuel: in all cases a homogeneous mixture was obtained, which may be compared to a true solution of organic sulfur compounds in a hydrocarbon medium. Separate particles of the solid phases are visible in the field of sight of the fuel mixtures with α -alkylthiophanes, di-isobutylsulfide, and ethylmethylcyclohexylsulfide. However, such particles are very small, and their dimensions are less than 0.1μ .

After heating the fuel mixtures and separating the solid particles visible at 100-magnification onto the filter, an entirely different picture was obtained. In the hydropurified fuel, solid particles, as before, were absent, but in the fuel with organic sulfur compounds an accumulation of particles of different density and magnitude were distinctly conspicuous. At a temperature of 200°C and a concentration of mercaptans of 0.01% (Fig. 3) the biggest accumulations of particles are formed in the form of dense aggregates, the dimensions of which exceed 1μ . Obviously, under these conditions the colloidal system formed during heating of the fuel mixture is destroyed and precipitates out in proportion to the size of the particles in the deposit.

*Work on the electron microscope was executed by B. I. Leont'yev and A. Ye. Sazonov.

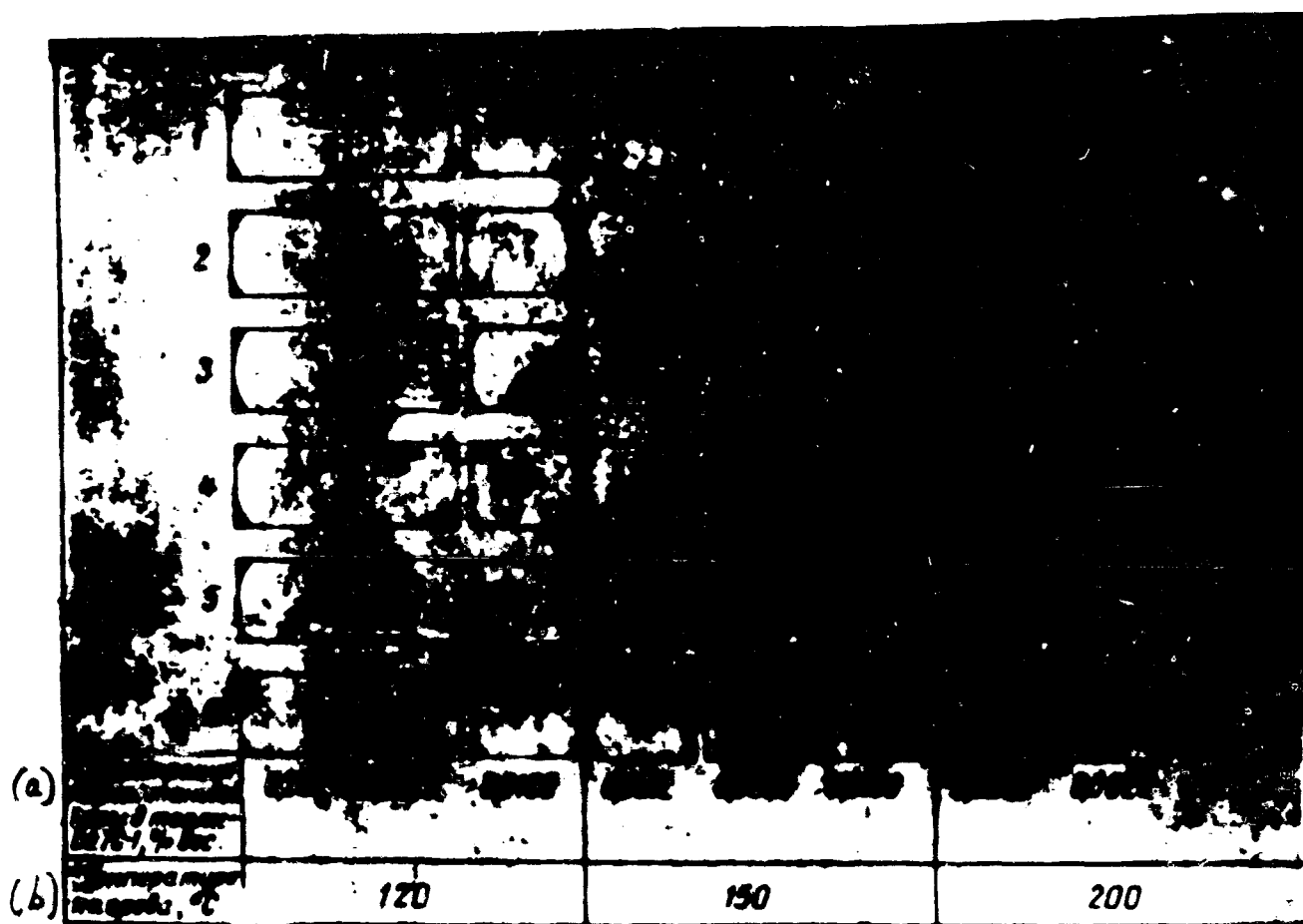


Fig. 3. Hydropurified fuel TS-1 with mercaptans after heating (magnified 10,000 times).

1—Fuel without mercaptans; 2—With isoamylmercaptan; 3—With secondary-octylmercaptan; 4—With methylcyclohexylmercaptan; 5—With benzylmercaptan; 6—With α -thionaphthol.

KEY: (a) Concentration of mercaptan sulfur in fuel TS-1, % weight; (b) Temperature of heating, °C.



Fig. 4. Hydropurified fuel TS-1 with 0.25% weight of sulfurous concentrates, sulfides, thiophanes, thiophenes, and disulfides (magnified 10,000 times).

a—Sulfurous concentrates and sulfides: 1—Sulfurous concentrate TS-1 ($t_k = 150-200^\circ\text{C}$; $S = 4.3\%$); 2—Sulfurous concentrate TS-1 ($t_k = 187-240^\circ\text{C}$; $S = 17.96\%$); 3—Dibutylsulfide; 4—Di-isobutylsulfide; 5—Ethylmethylcyclohexylsulfide.

b—Thiophenes, thiophanes, and disulfides: 1— α -amylthiophane; 2—Thiophene; 3— α -butylthiophane; 4—Di-secondary-octyldisulfide; 5—Di-o-tolylsulfide.

KEY: (a) Prior to heating.

The same picture is observed for a large part of the other organic sulfur compounds. Inasmuch as in the initial hydropurified fuel under these same conditions the formation of a colloidal system was not observed, and moreover, no precipitate, it is natural to consider that this process is caused by organic sulfur compounds.

For all of the compounds, besides the thiophenes, with an increase in the temperature of heating the quantity of particles of deposit visible under the microscope, the area occupied by them, and the density of their accumulations strongly increase (see Fig. 4). At 200-250°C in mixtures with thiophenes and disulfides the accumulations of the aggregate solid phase is so great that in separate cases particle dimensions exceed $1\ \mu$, i.e., it goes beyond the dimension limits of particles characteristic of a colloidal system. On photographs is shown the process of destruction of the colloidal system, accompanied by the enlargement and backing of particles with subsequent loss of the solid phase in deposit.

In the presence of thiophenes in fuel during heating of it to 250°C the solid particles precipitate in very small quantity and are of small dimensions (to $0.1\ \mu$); noticeable aggregating of the particles does not occur. In other words, thiophenes showed themselves to be the most thermally stable organic sulfur compounds, in the presence of which a stable colloidal system will be formed with minute solid phase particles.

Conclusions

1. Research on the influence of individual organic sulfur compounds of various structure on the exploitational properties of TS-1 type fuels in the case of a total content of sulfur within the limits, allowed by GOST 7149-54, showed that the corrosivity with respect to bronze of mercaptans, sulfides, thiophenes, and disulfides during heating of the fuel to a temperature of 200-250°C is small, with the exception of di-o-tolyldisulfide which is extremely corrosive.

2. Sulfides, disulfides and to a smaller degree, mercaptans of aromatic structure are a source of significant tar formation on metals during heating of fuel higher than 150°C. Thiophenes, during heating of fuel to 250°C, do not give tarry precipitates on bronze.

3. At 150-250°C acyclic and cyclical sulfides, thiophenes, and disulfides are a source of formation of significant quantities of deposits (which are insoluble in fuel), the quantity and magnitude of whose particles increase as the concentration of sulfurous compounds and the heating increase. In the presence of thiophenes and mercaptans (to 0.01%) and during heating of the fuel to 250°C the deposit is insignificant.

4. In standard fuels there is present a mixture of organic sulfur compounds of different structure; therefore, their influence on the exploitational properties of the fuels is levelled, which is proven by the results of tests with sulfurous concentrates of fuel TS-1.

5. The presently permissible norms of organic sulfur compounds in fuels of type T are limiting ones, i.e., they do affect the quality of the fuel when it is heated to 120°C. At a higher temperature it is necessary to take measures to prevent the negative influence of mercaptans, sulfides, thiophenes, and disulfides on the exploitational properties of fuels.

6. In the presence of thiophenes and its homologs during heating of fuel to 250°C its exploitational qualities are not lowered.

INFLUENCE OF NATURAL AND SYNTHETIC SULPHUR- AND NITROGEN-CONTAINING
COMPOUNDS ON THE THERMOOXIDIZING STABILITY OF DIRECT
DISTILLATION OF FUELS

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In directly distilled fuels of the kerosene type along with organic sulfur compounds nitrogen organic compounds are also present [1].

We separated sulfur- and nitrogen-containing compounds of a "basic" character from the tarry part of fuels TS-1, T-1, and DA. The method of separation was the following [2].

Tars were dissolved in sulfuric ether in a volumetric ratio of 1:1. The sulfur- and nitrogen-containing compounds from solution were extracted by treatment with a 25% aqueous solution of sulfuric acid. After settling, the acid layer was separated and passed through a paper filter, on which traces of tar were retained and then carried away by mechanical means. The filtrate was neutralized under strong cooling by a 30% solution of alkali up to a weakly alkaline reaction. The separated oily layer was extracted by sulfuric ether. The ether extract was dried by heated sodium sulfate. After distillation of the sulfuric ether there remained an oil, consisting of sulfur- and nitrogen-containing compounds of a "basic" character.

Extraction was continued until no more oil was extracted from the next fresh portion of acid solution. In separate cases such treatment of the tars was repeated up to 8 times.

In Table 1 are given the yield and characteristics of the separated compounds.

The results of investigation of the properties of separated sulfur- and nitrogen-containing compounds with the application of physicochemical and spectral methods make it possible to consider that these compounds can exert both a negative and positive action on the thermooxidizing stability of fuels [3, 4].

The determination of the thermooxidizing stability was conducted in a specially designed apparatus at a temperature of 150°C for 6 hours [5].

The fuel was in closed vessels in contact with bronze VB-24; the vessels were given an oscillatory motion by a crankgear. At the end of 6 hours, after cooling the instrument the corrosion of the bronze plate placed in the fuel was determined (g/m^2) and also the quantity of deposits on this plate (g/m^2) and of insoluble deposit in the fuel (milligram/100 ml).

The deposit was separated by filtration of the fuel through a No. 4 glass filter. The acidity (potentiometric) and optical density of the filtered fuel were determined. In process of the work the deposit and plate were photographed at 300 X magnification on a MDM-8 microscope.

All of the compounds studied in optimum concentrations somewhat improved the thermooxidizing stability of the initial detarred fuel.

Thus, during addition of separated compounds to detarred fuel TS-1 the corrosion and optical density were not changed practically, and the formation of insoluble deposit on the bronze decreased somewhat. At concentrations of 0.03-0.05% weight a minimum of sedimentation was clearly indicated (Fig. 1).

The variational curves of corrosion, sedimentation and optical density have distinct minima at the following concentrations of the investigated compounds:

0.05-0.09% for fuel DA (Fig. 2) and 0.02-0.06% - for fuel T-1 (Fig. 3). With an increase of the optimum quantity of sulfur- and nitrogen-containing compounds in the fuels, sedimentation, corrosion, and tar formation are increased.

Table 1. Physicochemical Properties of Sulfur- and Nitrogen-Containing Compounds Separated From Fractions of Fuel Tars.

Characteristics	Compounds separated from the alcohol-acetone fraction of tars of fuel TS-1	Fuel DA Fuel T-1			
		Compounds, separated from the fraction of tars			
		Benzene	Alcohol-acetone	Benzene	Alcohol-acetone
Yield, % weight per fraction of tars..	13.4	10.1	43.4	—	—
Molecular weight.....	193.5	243.1	602.4	210.1	232.4
Index of refraction n_D^{20}	1.5241	1.5209	1.5383	1.5248	1.5305
Density, g/cm ³	1.0039	1.0139	1.1010	1.0112	1.0935
Iodine number, g I per 100 g.....	31.4	36.7	49.3	40.1	38.4
Elementary composition, % weight:.....					
C.....	79.98	72.41	72.17	82.32	73.71
H.....	10.13	9.82	10.01	9.36	8.92
S.....	2.32	1.25	4.12	1.54	1.80
N.....	5.66	8.81	6.81	5.67	11.63
O (by difference).....	1.91	7.71	6.89	1.11	1.94
Ash.....	0.0021	0.0048	0.0072	0.0036	0.0051

The basic cause of increased thermooxidising stability of the fuels at optimum quantities of the studied compounds, apparently, must be considered to be the presence in the tarry part of the fuels of certain compounds, capable of forming a durable film on the surface of metal which "protects" the fuel from the catalytical influence of the metal. In connection with this there is a decrease in the quantity of insoluble deposit and tarry deposit formed. Furthermore, these compounds, probably, also have a certain inhibiting action on the process of the oxidation of the heated fuel by atmospheric oxygen.

To confirm this supposition experiments were conducted with individual, specially synthesized sulfur- and nitrogen-containing organic compounds, the

properties of which are given in Table 2 (in all 61 compounds). The results of studies of fuel TS-1 with additions of individual compounds are given in this same table.

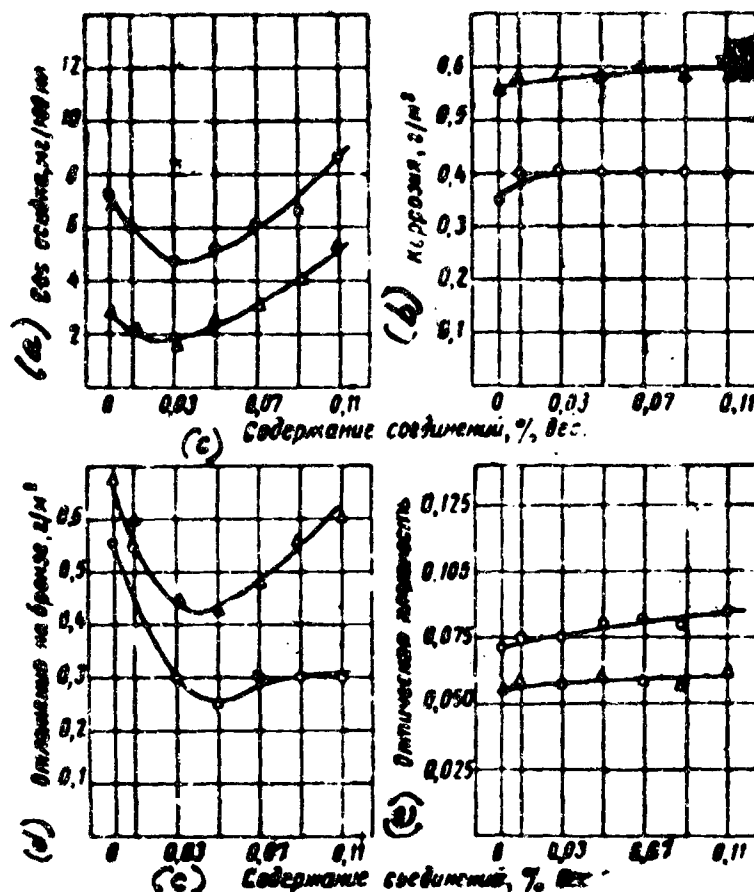


Fig. 1. Influence of sulfur- and nitrogen-containing compounds of a "basic" character on the thermooxidizing stability of fuel TS-1 (at a temperature of 150°C).

Δ - in glass vessels; O - in brass vessels.

KEY: (a) Weight of deposit, milligram/100 ml; (b) Corrosion, g/m²; (c) Content of compounds, % weight; (d) Deposit on bronze, g/m²; (e) Optical density.

All of the aminodisulfides lower the thermooxidizing stability of initial fuel TS-1 by 1.5-2 times. Aminosulfides with aliphatic radicals increase sedimentation and corrosion by 2-3 times. The formation of tarry deposits on bronze is increased insignificantly. Introduction of the phenyl radical (*p*-amino-ethylphenylsulfide) sharply decreases the sedimentation in fuel. Evidently, the phenyl radical plays an inhibiting role here.

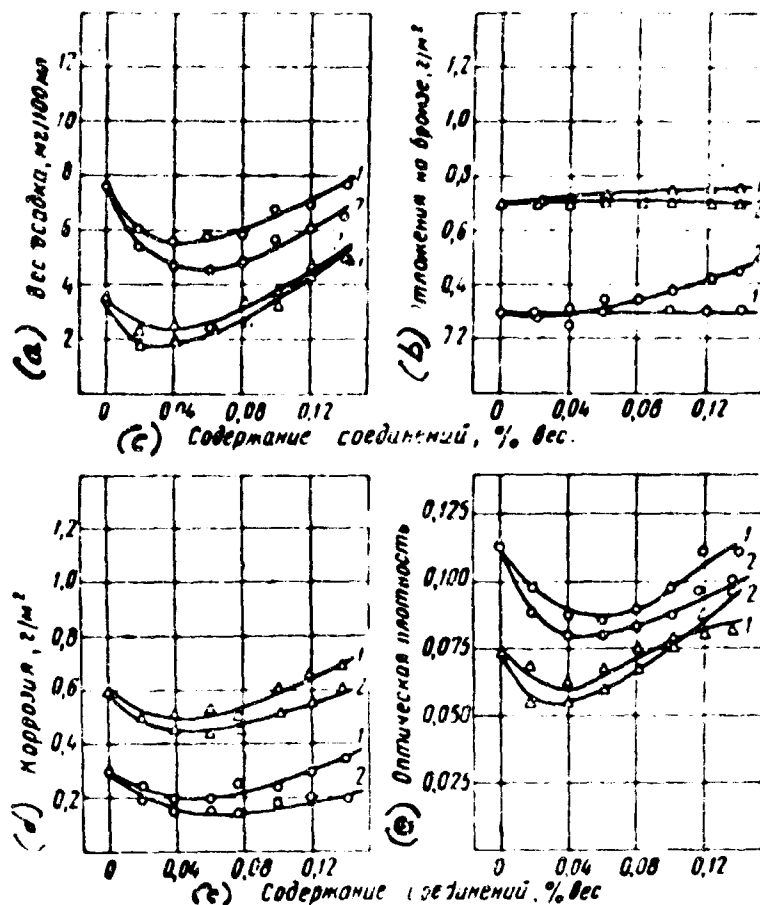


Fig. 2. The influence of sulfur- and nitrogen-containing compounds of a "basic" character [separated from benzene (1), and alcohol-acetone (2) fractions of tars] on the thermooxidizing stability of fuel DA (at a temperature of 150°C).

Δ - in glass vessels; O - in brass vessels.

KEY: (a) Weight of deposit, milligram/100 ml; (b) Deposit on bronze, g/m²; (c) Content of compounds, % weight; (d) Corrosion, g/m²; (e) Optical density.

In our preceding work [6] it was shown that mercaptans significantly lower the exploitational properties of fuels. It was of interest to investigate how the amine group influences these properties of mercaptans. Of 7 synthesized aminothiols, 6 showed unsatisfactory properties from the point of view of their influence on the thermooxidizing stability of the fuels. One of the aminothiols (2-phenyl-2-mercaptobutylamine) significantly improves the stability of the fuel: in its presence almost no deposit was formed in the fuel.

Aminonitriles differ little in stability - they are easily disintegrated and form peroxide radicals. This, evidently, was also a basic cause of the lowered

thermal stability of the fuel during addition of aminonitriles, especially with respect to deposit- and tar formation.

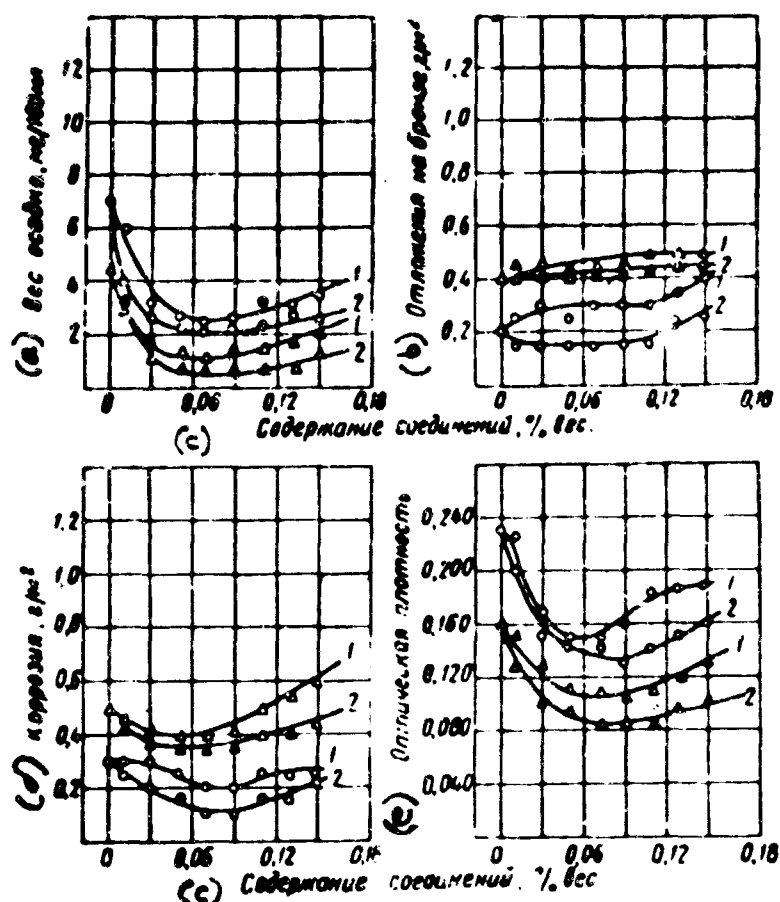


Fig. 3. Influence of sulfur- and nitrogen-containing compounds of a "basic" character [separated from benzene (1) and alcohol-acetone (2) fractions of tars] on the thermooxidizing stability of fuel T-1 (at a temperature of 150°C).

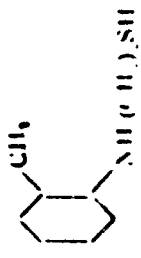
Δ - in glass vessels; O - in brass vessels.

KEY: (a) Weight of deposit, milligram/100 ml; (b) Deposit on bronze, g/m²; (c) Content of compounds, % weight; (d) Corrosion, g/m²; (e) Optical density.

All of the investigated thiazolidines and thiazolines increase the sedimentation and corrosion of fuel, but some of them (*γ*-phenylthiazolidine and 2-n-hydroxyphenylthiazolidine) decrease the corrosion of bronze by 4 times as compared to the initial fuel.

Ascomethynes prevent the depositing of insoluble tars on bronze, but all ascomethynes, with the exception of *o*-phenylene diamine and salicylal-*o*-aminophenol, lower thermal stability of the fuel with respect to sedimentation and corrosion of the metal.

Table 2. Physico-chemical Properties of Synthesized Sulfur- and Nitrogen-Containing Compounds and the Influence of Additions of these Compounds (0.05% weight) on the Thermooxidizing Stability of Fuel TS-1.

Structural formula	Designation of compound	Physico-chemical properties					Influence on fuel TS-1		
		Boiling point, °C (pressure, mm Hg cm)	η_{sp}^0	Calcd	Found	Deposits, %	Corrosion, %	Deposit on 100 Hrs	Deposit on 100 Hrs
Initial fuel TS-1	—	—	—	—	—	—	2.6	0.5	0.5
1. <u>Aminodisulfides</u>									
$[(CH_3)_2N(CH_2)_2S-]_2$	Bis (N-dimethyl-β-aminoethyl) disulfide	120-125 (5)	0.9852	1.5109	1.5124	—	5.9	0.9	0.6
$[(C_4H_9)_2N(CH_2)_2S-]_2$	Bis (N-diethyl-β-aminoethyl) disulfide	115 (5)	0.572	1.5440	1.5430	81.11	3.6	0.9	3.2
$[(CH_3)_2N(CH_2)_2S-]_2$	Bis (N-dimethyl-β-amino-propyl) disulfide	Is decomposed during distillation				—	4.9	2.2	1.5
2. <u>Aminosulfides</u>									
$C_4H_9S(CH_2)_2NH_2$	β-Aminoethylethylsulfide	103	0.9533	1.4922	1.478	21.06	6.2	1.0	1.1
$C_4H_9S(CH_2)_2NH_2$	β-Aminoethyl-n-butylsulfide	106-108 (50)	0.9178	1.5060	1.502	31.28	9.2	1.1	1.6
$C_4H_9S(CH_2)_2NH_2$	β-Aminoethylphenylsulfide	135 (50)	0.8245	1.5922	1.595	37.68	1.7	1.1	1.2
$(C_4H_9)_2N(CH_2)_2SC_4H_9$	N-Diethyl-β-aminoethyl-butylsulfide	95 (50)	0.8710	1.4970	1.4901	39.35	10.5	1.9	3.6
3. <u>Aminoethiol</u>									
	N-β-Mercaptoethylamine-O-toluidine	180 (5)	—	1.5892	—	—	3.5	1.2	2.1

(Table 2 continued)

$ \begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C} \\ \quad \\ \text{CH}_2\text{NH}_2 \quad \text{SH} \\ \\ \text{C}_6\text{H}_5 \\ \\ \text{C}_6\text{H}_5\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH})_2 \end{array} $	2-Phenyl-2-mercaptobutyl-amine	120 (5)	1,0507	1,4250	55.85	74.90	0.5	0.1	0.2
$ \begin{array}{c} \text{C}_6\text{H}_5 \\ \\ \text{C} \\ \quad \\ \text{CH}_2\text{SH} \quad \text{SH} \\ \\ \text{C}_6\text{H}_5\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH})_2 \end{array} $	N-Cyclohexyl-bis (2-mercaptopropyl) amine	157 (6)	1,0182	1,5270	73.5	71.0	9.8	6.1	2.0
$ \begin{array}{c} \text{C}_6\text{H}_5\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH})_2 \\ \\ \text{SH} \end{array} $	N-Phenyl-2-mercaptopropyl-amine	95 (5)	0,9515	1,5004	—	—	3.5	0.9	1.5
$ \begin{array}{c} \text{CH}_3\text{—N} \\ \\ \text{CH}_3\text{—C—SH} \\ \\ \text{CH}_3 \end{array} $	2-Mercaptothiazoline	106—107 *	—	—	—	—	1.0	2.9	5.9
$ \begin{array}{c} \text{CH}_2\text{SH} \\ \\ \text{CH}_2\text{—O—CH}_2\text{—CH}_2\text{—SH} \end{array} $	2-Furfurylmercaptan	138 (7.4)	—	1,5322	—	—	1.6	27.0	315.0
$ \begin{array}{c} \text{CH}_2\text{—CH}_2\text{—SH} \\ \\ \text{CH}_2\text{—N—CH}_2\text{—CH}_2\text{—SH} \\ \\ \text{CH}_2\text{—O—CH}_2\text{—CH}_2\text{—SH} \end{array} $	N-bis-(β -mercaptoethyl)-furfuralamine	146 (5)	1,1430	1,5496	61.50	60.45	5.7	0.6	0.7
4. Aminonitriles									
$ \begin{array}{c} \text{H}_2\text{N}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{CH}_2\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ (\text{CH}_2)_4\text{N}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{C}_6\text{H}_{11}\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \end{array} $	β -Aminopropionitrile	85—87 (22—25)	—	1,4340	—	—	4.5	0.5	0.8
$ \begin{array}{c} \text{H}_2\text{N}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{CH}_2\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ (\text{CH}_2)_4\text{N}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{C}_6\text{H}_{11}\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \end{array} $	N-Methyl- β -aminopropionitrile	74—81 (20—25)	—	1,4270	—	—	7.0	1.5	1.0
$ \begin{array}{c} \text{H}_2\text{N}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{CH}_2\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ (\text{CH}_2)_4\text{N}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{C}_6\text{H}_{11}\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \end{array} $	N-Dimethyl- β -aminopropionitrile	10.9	—	1,4230	—	—	12.0	1.0	0.7
$ \begin{array}{c} \text{H}_2\text{N}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{CH}_2\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ (\text{CH}_2)_4\text{N}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{C}_6\text{H}_{11}\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \end{array} $	N-Benzyl- β -aminopropionitrile	167 (7)	1,0231	1,5263	48.19	58.02	5.6	1.1	0.7
$ \begin{array}{c} \text{H}_2\text{N}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{CH}_2\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ (\text{CH}_2)_4\text{N}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{C}_6\text{H}_5\text{CH}_2\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \\ \\ \text{C}_6\text{H}_{11}\text{NH}(\text{CH}_2)_4\text{C}\equiv\text{N} \end{array} $	N-Cyclohexyl- β -aminopropionitrile	126 (7)	0,9400	1,4723	41.88	44.88	4.5	0.3	0.5
$ \begin{array}{c} \text{CH}_2\text{—CH}_2\text{—C}\equiv\text{N} \\ \quad \\ \text{CH}_2\text{—CH}_2\text{—C}\equiv\text{N} \end{array} $	N-Cyclohexylhydroxylaminonitrile	127—128 *	—	—	—	—	4.5	0.3	0.5
5. Thiazolidines and thiazolines									
$ \begin{array}{c} \text{CH}_2\text{—N—C}_6\text{H}_5 \\ \quad \\ \text{CH}_2\text{—C—C}_6\text{H}_5 \\ \quad \\ \text{CH}_2\text{—CH}_2\text{—C}_6\text{H}_5 \end{array} $	2-Methyl-2-phenyl-3-phenylthiazolidine	—	—	—	—	—	5.0	1.1	1.2

*Temperature of fusing in °C.

(Table 2 continued)

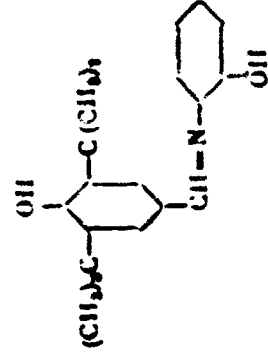
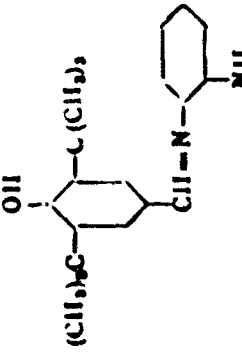
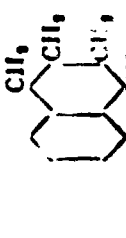
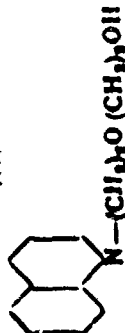
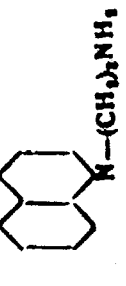
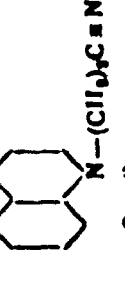
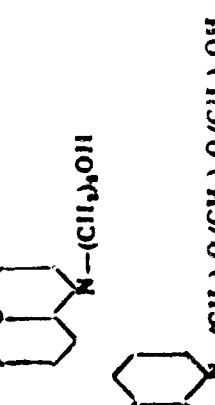
$ \begin{array}{c} \text{CH}_3-\text{N}-\text{C}_6\text{H}_5 \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{C} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{S} \end{array} $	2-Dimethyl-3-phenylthiasolidine	160-165	1.0164	1.5100	31.38	31.42	3.9	1.0	2.0
$ \begin{array}{c} \text{CH}_3-\text{NH} \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{C} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{S} \end{array} $	2-Dimethylthiasolidine	160-165	1.0164	1.5100	31.38	31.42	3.0	0.5	1.5
$ \begin{array}{c} \text{CH}_3-\text{NH} \\ \quad \\ \text{CH}_2 \quad \text{H} \\ \quad \\ \text{C} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{S} \end{array} $	2-Phenylthiasolidine	101*	—	—	—	—	0.0	0.4	0.8
$ \begin{array}{c} \text{CH}_3-\text{N}-\text{C}_6\text{H}_5 \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{C} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{S} \end{array} $	3-Phenylthiasolidine	31-31.5*	—	—	—	—	3.7	0.1	0.1
$ \begin{array}{c} \text{CH}_3-\text{NH} \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{C} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{S} \end{array} $	2-Methylthiasolidine	160-165	1.0561	1.5225	29.77	29.82	4.6	0.5	0.7
$ \begin{array}{c} \text{CH}_3-\text{NH} \\ \quad \\ \text{CH}_2 \quad \text{CH}-\text{C}_6\text{H}_4-\text{OH} \\ \quad \\ \text{C} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{S} \end{array} $	2-n-Oxyphenylthiasolidine	—	—	—	—	—	3.0	3.0	0.1
$ \begin{array}{c} \text{CH}_3-\text{N} \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{C} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{S} \end{array} $	2-γ-Pyridylthiasolidine	135-140 (3)	1.2130	1.6070	40.71	40.97	2.8	1.0	1.0
$ \begin{array}{c} \text{CH}_3-\text{NH} \\ \quad \\ \text{CH}_2 \quad \text{C}-(\text{CH}_2)_2\text{N}(\text{CH}_2)_2 \\ \quad \\ \text{C} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{S} \end{array} $	2-(N-dimethyl)-β-aminoethylthiasolidine	114-117 (3)	1.1561	1.5580	45.07	41.07	4.8	2.0	0.2
$ \begin{array}{c} \text{CH}_3-\text{N} \\ \quad \\ \text{CH}_2 \quad \text{C}-(\text{CH}_2)_2\text{NHCH}_2 \\ \quad \\ \text{C} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{S} \end{array} $	2-(N-methyl)-β-aminoethylthiasolidine	130-132 (3)	1.1652	1.5546	40.6	39.4	0.8	1.5	1.1

*Temperature of fusing in °C.

(Table 2 continued)

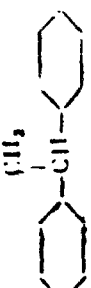
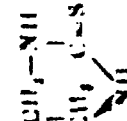
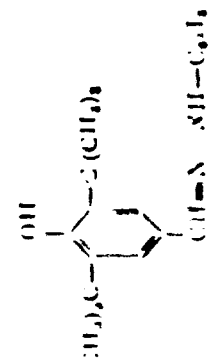
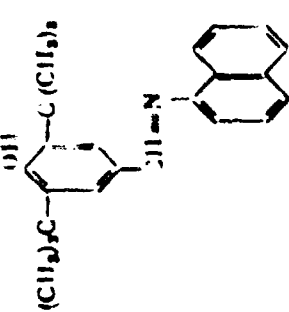
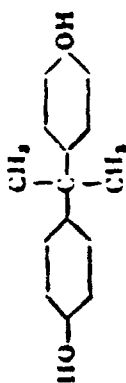
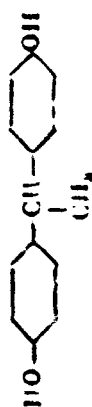
$\begin{array}{c} \text{CH}_3-\text{C}-\text{N} \\ \quad \\ \text{H} \quad \text{H} \\ \quad \\ \text{OH} \quad \text{C}-\text{NH}_2 \\ \quad \\ \text{C} \quad \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \end{array}$	2-Amino-4-methylthiazole	107 mμ		15.1	0.6	0.7
	6. Azomethynes					
$\begin{array}{c} \text{NH}_2 \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{OH} \\ \\ \text{N} \\ \\ \text{C}_6\text{H}_4 \end{array}$	o-phenylene diamine	103-104		1.1	0.3	0.5
$\begin{array}{c} \text{NH}_2 \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{OH} \\ \\ \text{N} \\ \\ \text{C}_6\text{H}_4 \end{array}$	Benzylal-o-aminophenol	89		2.1	0.1	1.2
$\begin{array}{c} \text{HO} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{OH} \\ \\ \text{N} \\ \\ \text{C}_6\text{H}_4 \end{array}$	Salicylal-o-aminophenol	176		0.9	0.2	1.0
$\begin{array}{c} \text{CH}_3 \\ \\ \text{N} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{CH} \\ \\ \text{N} \\ \\ \text{C}_6\text{H}_4 \end{array}$	n-N-Dimethylamino-benzylal-o-aminophenol	110		2.3	0.3	1.2
$\begin{array}{c} \text{NH}_2 \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{OH} \\ \\ \text{N} \\ \\ \text{C}_6\text{H}_4 \end{array}$	Benzylal-o-phenylene diamine	61-62		4.3	0.3	0.7
$\begin{array}{c} \text{NH}_2 \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{OH} \\ \\ \text{N} \\ \\ \text{C}_6\text{H}_4 \end{array}$	Solicylal-o-phenylene diamine	153		2.1	0.2	0.5
$\begin{array}{c} \text{NH}_2 \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{OH} \\ \\ \text{N} \\ \\ \text{C}_6\text{H}_4 \end{array}$	n-N-Dimethylamino-benzylal-o-phenylene diamine	125		11.5	0.2	0.5
	7. Lonol and its derivatives					
$\begin{array}{c} \text{HO} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{C}(\text{CH}_3)_2 \\ \\ \text{C}_6\text{H}_4 \end{array}$	3,5-di-tertiary-butyl-n-cresol	72		2.0	1.5	3.2
$\begin{array}{c} \text{OH} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{C}(\text{CH}_3)_2 \\ \\ \text{C}_6\text{H}_4 \end{array}$	3,5-di-tertiary-butyl-4-oxybenzaldehyde	188-190		1.1	0.3	0.7

(Table 2 continued)

	3,5-di-tert-butyl-4-hydroxybenzylal-o-aminophenol	170-171				
	3,5-di-tert-butyl-4-hydroxybenzylal-o-phenylene diamine	180		12.0	0.5	0.5
    	<p>8. Tetrahydroquinoline and its derivatives</p> <p>1,2,3,4-Tetrahydroquinoline</p> <p>N-(gamma-aminopropyl)-1,2,3,4-tetrahydroquinoline</p> <p>N-(beta-cyanoethyl)-1,2,3,4-tetrahydroquinoline</p> <p>N-(beta-ethoxy)-1,2,3,4-tetrahydroquinoline</p> <p>—</p>	<p>125-136 (15-25)</p> <p>167-170 (4)</p> <p>137-140 (4)</p> <p>195-210 (5)</p> <p>140-144 (5)</p> <p>205-207 (5)</p>	<p>1625, 15833</p> <p>1,1055, 1,5523, 63,44</p> <p>1,0450, 1,5777, 50,1</p> <p>1,0850, 1,5740, 55,57</p> <p>1,1041, 1,5740, 52,60</p> <p>1,1053, 1,5420, 71,42</p>	<p>—</p> <p>2.5</p> <p>4.9</p> <p>2.0</p> <p>3.7</p> <p>2.2</p>	<p>0.3</p> <p>0.4</p> <p>0.1</p> <p>0.2</p> <p>0.9</p> <p>3.3</p>	<p>0.2</p> <p>0.5</p> <p>0.2</p> <p>0.2</p> <p>0.3</p> <p>0.2</p>

(Table 2 continued)

9. Others

$C_{12}H_{11}N(CH_3)_2NiCl_2$  	N,N'-diphenylethylenediamine Reaction product of styrene with phenol (the exact formula is not established) 2-Thioimidazoline						0.5	0.5	0.4
	3,5-di-tert-butyl-4-oxybenzylalphenylhydrazones	100-105°					0.6	0.6	1.0
	2-di-tert-butyl-4-hydroxybenzylal-α-naphthylamine	125-128°					0.3	0.3	1.3
	4,4'-Dioxydiphenylpropane	152-153°					0.3	0.3	1.3
	4,4'-Dioxydiphenylethane	122°					0.3	0.3	1.2

*Temperature of fusing in °C.

(Table 2 continued)

$(CH_3)_2C(OH)CH_2CH(OH)CH_2CH_2N(CH_2CH_2OH)_2$	N,N-Diallyl-N'-allyl-2-hydroxypropylene diamine	mm*	—	—	—	12.0	0.5	0.3
$[(C_2H_5)_2NCH_2CH(OH)CH_2]_2N(CH_2)_2OH$	Bis[3-(N,N-diethylamine)-2-hydroxypropyl]-β-hydroxyethylamine	15 (80)*	—	—	—	3.5	1.3	1.0
$[C_6H_4(NCH_2CH_2OH)]_2NCH_2CH_2OH$	Bis-(3-piperidyl-2-hydroxypropyl) amine	mm*	—	—	—	5.0	0.9	0.3
$(C_2H_5)_2NCH_2CH(OH)CH_2CH_2N(CH_2CH_2OH)_2$	N,N-Diethyl-N'-(3-piperidyl-2-hydroxypropyl)-2-hydroxypropylenediamine	mm*	—	—	—	1.4	0.4	0.9
$C_6H_5N(CH_2CH_2OH)_2N(CH_2CH_2OH)_2$	N,N-Diethyl-2-hydroxypropylenediamine	15 (10)*	—	—	—	5.4	1.3	0.5
$C_6H_5N(CH_2CH_2OH)_2N(CH_2CH_2OH)_2$	N,N-Diethyl 2-hydroxypropylenediamine	15 (10)*	—	—	—	6.0	1.0	0.7

*Temperature of fusing in °C.

Ionol derivatives (3,5-tert,-but-2-hydroxybenzaldehyde and 3,5-di-tert-butyl-4-hydroxybenzylal-o-aminophenol) effectively decrease sedimentation in fuel. Corrosion and the formation of tars which are insoluble in fuel remain almost the same as in the initial fuel.

Of the tetrahydroquinoline group, tetrahydroquinoline itself significantly improves exploitative properties of fuel being considered.

The product obtained by condensation of styrene with phenol improves the thermooxidizing stability of the fuel being investigated.

Thus, in the presence of certain sulfur- and nitrogen-containing compounds which have been synthesized and separated from fuels, the thermooxidizing stability of fuel is increased. The substances which have an inhibiting action are complicated heterocyclic compounds, characterized by the presence of atoms of nitrogen in a ring, sulfur in the form of the thiol group, and oxygen in the form of a hydroxyl group.

Conclusions

1. Synthetic sulfur- and nitrogen-containing organic compounds basically lower thermooxidizing stability of directly distilled fuels, with the exception of 2-phenyl-2-mercaptobutylamine, 1,2,3,4-tetrahydroquinoline; certain derivatives of ionol; and the product, obtained by the interaction of styrene with phenol.

2. In tars of fuels TS-1, T-1, and DA are contained compounds, which in small concentrations are able to improve effectively the thermooxidizing stability of fuels. These are basically - heterocyclic compounds, containing thiol, amine, and phenyl groups.

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INVESTIGATION OF THE THERMAL STABILITY AND CORROSIVENESS OF SULFUROUS FUELS AT TEMPERATURES ABOVE 100°C

Ye. R. Tereshchenko and M. Ye. Tararyshkin

The length of service and reliability of work of motors depend to a significant degree on the quality of fuel used and primarily on its thermal stability and corrosiveness.

Motor operational experience shows that standard fuel TS-1 obtained from eastern sulfurous crudes, at operating temperatures higher than 100°C will form insoluble sediments, which are deposited on the components of fuel equipment. Cases are also noted of heightened corrosional wear of fuel pumps components, burner nozzles, and filters during operation of motors on such fuel.

In 1960 we conducted research to study the thermal stability and corrosiveness of sulfurous fuels at temperatures above 100°C.

The following sulfurous fuels were tested: TS-1 hydropurified fuel, TS-1 with a heightened content of mercaptan sulfur obtained from a mixture of Stavropol' and Chapayovsk crudes, TS-1 with a heightened content of sulfur, obtained from arlan-chekmagush crude, and also standard fuels TS-1 and T-1 (Table 1).

The thermal stability and corrosiveness of sulfurous fuels were studied under static conditions in a bomb and in a flow during a single-time injection of fuel on a device simulating the work of the fuel filter of a motor [1].

Table 1.

Fuel	Density ρ_{4}^{20}	Limits of boiling out, °C	Group chemical composition, %			Sulfur, %	Mercaptans, %	Actual tars, milligram/100 ml
			Paraffin	Naphthene	Aromatic			
TS-1 hydropurified...	0.778	137—235	60.00	24.00	16.00	0.01	0.000	0.0
TS-1 from mixture of Stavropol' and Chapayevsk crudes...	0.778	133—228	—	—	13.80	0.16	0.030	7.0
TS-1 from arlan- chekmagush crude....	0.782	142—232	—	—	14.40	0.47	0.002	5.0
TS-1.....	0.778	133—230	56.00	25.50	18.50	0.20	0.009	2.4
T-1.....	0.818	139—278	20.70	62.90	16.40	0.06	0.000	1.6

The research conditions for fuel in a bomb correspond to the conditions in a fuel tank, which makes it possible to determine the total amount of insoluble deposits and tars and the corrosion of fuel equipment components under static conditions. Research on fuels in flow simulates the work of a fuel system beyond the tank and makes it possible to estimate the influence of insoluble deposits and tars on the working of fuel filters and the corrosion of fuel equipment components under dynamic conditions.

Necessity of such a double appraisal of fuels is unavoidable since the reliability of work and service life of a fuel system depend on both the total quantity of deposits and tars forming in the fuel and on their ability to be deposited on fuel equipment parts and filters. The study of corrosion is particularly important for fuels containing active sulfur.

The results of research on the thermal stability of sulfurous fuels under static conditions in a bomb at a temperature of 150°C are given in Table 2.

Table 2.

Fuel	Quantity of deposit, mg/100 ml of fuel		Quantity of tars, mg/100 ml of fuel	
	without metal	with bronze	without metal	with bronze
TS-1 hydropurified..	1.0	8.0	8.0	10.6
TS-1 from a mixture of Stavropol' and Chapayevsk crudes..	1.3	23.4	9.8	13.6
TS-1 from arlan-chekmagush crude...	18.9	33.1	41.6	35.6
TS-1.....	5.3	18.5	15.2	21.6
T-1.....	29.4	34.0	17.6	30.8

The data of Table 2 show that fuel TS-1 which has been subjected to hydropurification has the best thermal stability. Consequently, hydropurification is an effective method of increasing the thermal stability of fuels obtained from eastern sulfurous crudes.

Fuel obtained from arlan-chekmagush crude turned out to be the most unstable. During heating it will form a significant quantity of insoluble deposits and tars. Fuel TS-1 obtained from mixture of Stavropol' and Chapayevsk crudes, possesses sufficiently high thermal stability during heating without metal, but in the presence of bronze the quantity of insoluble deposits in it sharply increases.

Analysis of the deposits obtained during test of sulfurous fuels in the bomb, showed that these deposits contain a large quantity of ash (to 20% and above). It was noted that the higher the active sulfur content (mercaptans and elementary sulfur) the higher the ash content of the deposits. This circumstance makes it possible to suppose that heightened formation of insoluble deposits is connected with the corrosion of bronze and loss of products of corrosion in solid phase.

From the data, given in Table 2, it is also clear that standard fuels TS-1 and T-1 possess insufficient thermal stability, especially fuel T-1.

In Fig. 1 are shown the results of analysis of the thermal stability of sulfurous fuels under dynamic conditions at a temperature of 150°C for 5 hours (with single fuel injection through the filter). The criteria for analysis of the thermal stability of fuels were the pressure drop on the filter, the characteristic degree of clogging of the filter by insoluble deposits, and the state of filter after the test.

Fuel TS-1 after being subjected to hydropurification under the indicated conditions does not clog the filter with deposits. Standard fuels TS-1 and T-1 are unstable: complete clogging of the filter with insoluble deposits for fuel T-1 occurs after 2 hours, 20 minutes, and for fuel TS-1 - after 4 hours, 30 minutes. The character of the filter clogged by insoluble deposits is shown in Fig. 2.

Sulfurous fuels TS-1 from arlan-chekmagush crude and TS-1 from a mixture of Stavropol' and Chapayevsk crudes have a significantly smaller inclination to clog the filter than do standard fuels TS-1 and T-1, although under static conditions in a bomb these fuels were practically equivalent to standard fuels TS-1 and T-1. This is explained by the fact that the deposits forming in these fuels have smaller particles and, therefore, are not stopped by the filter.

Consequently, sulfurous fuels, depending upon their chemical composition, form during heating insoluble deposits which can be distinguished both by quantity and by quality (size of particles).

Deposits forming in sulfurous fuels during their heating above 100°C are amorphous carbon particles usually black and sometimes dark-brown.

In Fig. 3 are shown photomicrographs of fuels TS-1 and T-1 at 120X magnification after heating in a bomb at a temperature of 175°C for 4 hours.

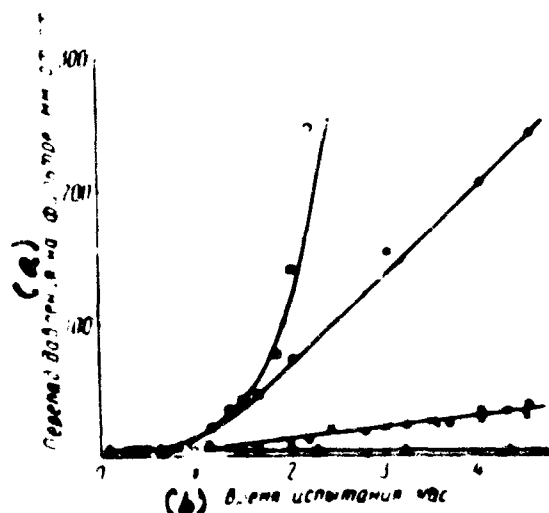


Fig. 1. Characteristic of filter clogging by insoluble deposits during a single injection of sulfurous fuels.

Δ - TS-1 hydrorefined; X - TS-1 from mixture of Stavropol' and Chapayevsk crudes; O - TS-1 from arlan-chekmagush crude; ● - TS-1 standard; □ - T-S standard.

KEY: (a) Pressure drop on filter, mm Hg; (b) Time of test, hours.

A method of screen analysis was applied to determine the particle size of the deposits formed in sulfurous fuels. Results of the analysis (Fig. 4) showed that the deposits of standard fuels TS-1 and T-1 have bigger particles; 75-80% of these deposits were trapped by a 20 μ filter. Deposits of fuel TS-1 from the mixture of Stavropol' and Chapayevsk crudes have the smallest particles - 75% of these deposits were trapped by a filter of only less than 5 μ size.

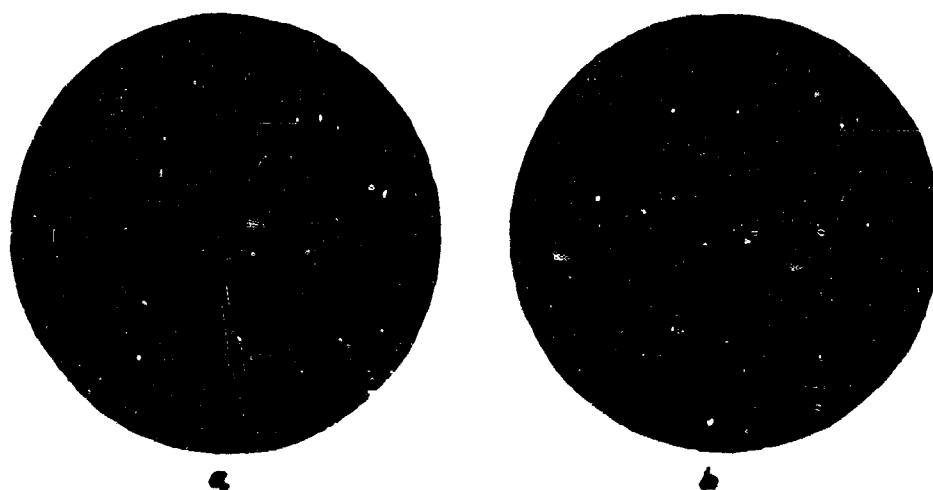


Fig. 2. Appearance of filter before (a) and after (b) test with standard sulfurous fuel TS-1.

The magnitude of the deposit particles of sulfurous fuels significantly increased during testing in contact with bronze (Fig. 5). Thus, 75% of TS-1 fuel deposits are trapped by a 20 μ filter during testing of this fuel in contact with bronze; 72% of the deposits formed are trapped on even a 60-micron filter. Thus,

bronze not only increases the inclination of sulfurous fuels to sedimentation, but also evokes a size increase in the particles of the deposits formed. The influence of bronze on the magnitude of particles of low-sulfur fuel T-1 is in the opposite direction: the size of deposit particles decreases. Steel has practically no influence on the magnitude of deposit particles formed in either sulfurous or in low-sulfur fuels.

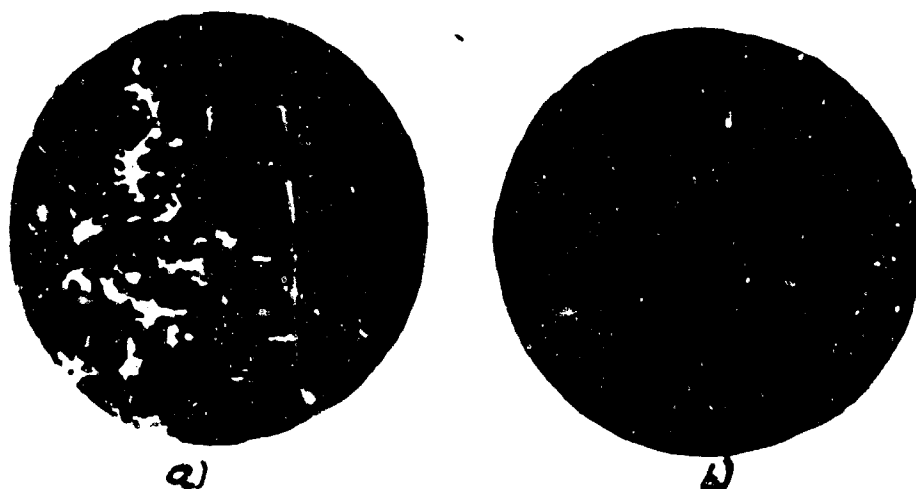


Fig. 3. Photomicrographs of fuel TS-1 a) and T-1 b) after heating.

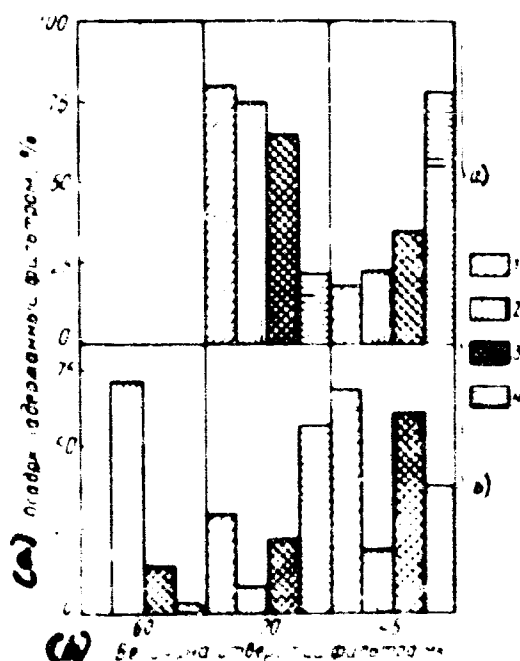


Fig. 4. Particle size of sulfurous fuel deposits during test with bronze b) and without it a).
 1—T-1 standard; 2—TS-1 standard;
 3—TS-1 from arlan-chekmagush crude;
 4—TS-1 from mixture of Stavropol' and Chapayevsk crudes.
 KEY: (a) Deposit trapped by filters, %;
 (b) Magnitude of filter holes, μ.

In Table 3 is given the chemical composition of insoluble deposits obtained during testing of fuels TS-1 and T-1 in a bomb at a temperature of 175°C.

The chemical composition of the deposits makes it possible to suppose that they are formed in fuels TS-1 and T-1 as a result of the oxidation by atmospheric oxygen of thermally unstable sulfur-nitrogen, and oxygen-containing organic compounds, which are present in the fuel.

Our experiments showed that if from fuel T-1 or TS-1 the dissolved air were removed and it was heated in special ampoules, then in the temperature interval 100-250°C deposits and tars will not be formed in the fuel.

Table 3.

Fuel	Chemical composition of deposits, %					
	C	H	N	S	O	Ash
TS-1.....	64.80	5.78	4.18	6.76	18.48	None
TS-1 in contact with bronze.....	46.97	4.84	2.46	8.06	13.35	24.32
T-1.....	67.53	6.83	1.91	5.92	16.10	1.71
T-1 in contact with bronze.....	62.62	5.23	0.7	6.09	18.00	7.14

A peculiarity of the influence of temperature on the formation of insoluble deposits in hydrocarbon fuels is the presence of a maximum in a definite region of temperature.

Under both static and dynamic test conditions the maximum formation of insoluble deposits is within the same limits. Thus, in the bomb the maximum quantity of deposits will be formed in the temperature interval 150-200°C; in practically the same range of temperatures there is observed a maximum speed of growth of the pressure drop on the filter or speed of clogging in the filter by insoluble deposits.

At present there is no universally recognized explanation of the temperature maximum for insoluble deposit formation in hydrocarbon fuels. Different authors have given a number of suggestions concerning this question [2, 3].

Visual observations of the formation of deposits in fuel in special apparatus have shown that during heating of the fuel above 100°C it first becomes slightly cloudy, then the finest particles appear in the form of white dots. With further heating these particles gradually grow, acquiring a brown and then a black color. Subsequently, agglomeration of particles occurs (see Fig. 5). At temperatures above

175°C the quantity of particles gradually decreases, and at a temperature of 250°C only a small quantity of big particles remains.



Fig. 5. Particle-agglomerate of fuel TS-1 deposit at 120X magnification.

Visual observations and experimental determinations of the temperature dependent sedimentation in fuels makes it possible to explain temperature maximum of insoluble deposit formation in the following form.

With increase of temperature of heating of fuel as a result of oxidation by atmospheric oxygen of the unstable impurities of the fuel (sulfur-, nitrogen-, and oxygen-containing organic compounds

and unsaturated hydrocarbons) at the beginning of oxidation tars dissolved in the fuel are formed. In certain cases part of these high-molecular tars may precipitate at temperatures of 100-130°C. With further increase of the temperature condensation and packing of the molecules occurs, and the final products of oxidation are formed - insoluble deposits. At temperatures of 175-250°C a large part of the deposits formed (80-90%) is dissolved in fuel; then, apparently under the influence of temperature their thermal disintegration begins with the formation of light oxidation products which do not precipitate into the solid phase. At temperatures above 250°C there remains in the fuel only a small condensed and consolidated part of the deposit.

The corrosiveness of sulfurous fuels was studied by many researchers, and in this region there has recently been published a number of works. However, these investigations were conducted at temperatures below 100°C.

We investigated the corrosiveness of sulfurous fuels at a temperature of 150°C under static conditions in a bomb and under dynamic conditions on apparatus, simulating the operation of a fuel filter of a motor (Table 4).

Table 4.

Fuel	Loss in weight of plates, g/m ²		
	Under static conditions (in bomb)		Under dynamic conditions (on apparatus)
	Steel	Bronze	Bronze
TS-1 hydropurified.	0.00	0.25	0.60
TS-1 from arlan-chekmagush crude..	—	0.99	1.80
TS-1 standard.....	0.24	1.50	7.05
TS-1 from mixture of Stavropol' and Chapayevsk crudes.	1.29	3.07	42.40

Fuel TS-1 which has been subjected to hydropurification has the least corrosiveness. As compared to standard fuel TS-1 its corrosiveness is less by approximately 10 times. The most corrosive is fuel TS-1 from a mixture of Stavropol' and Chapayevsk crudes, which contain 0.03% mercaptan sulfur.

Conclusions

1. Insoluble deposits in sulfurous fuels of type TS-1 are formed at temperatures above 100°C. The biggest inclination of these fuels to sedimentation is observed in the temperature interval 150-200°C.

2. Deposits forming in sulfurous fuels are products of oxidation mainly of the sulfur, - nitrogen, - and oxygen-containing organic compounds present in these fuels.

3. Hydropurification of sulfurous fuels effectively increases their thermal stability and sharply lowers their corrosiveness. The quantity of deposits formed decreases by 2-3 times, and the corrosiveness is lowered by 10 or more times.

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